On the temperature dependence of the integrated intensity of the collision-induced fundamental band of O₂–O₂

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The temperature dependence of the integrated intensity of the collision-induced fundamental band of O₂–O₂ pairs has been investigated. For $T < 280$ K, most of the intensity has been shown to arise through the long-range isotropic quadrupolar mechanism, which leads to a monotonic decrease with increasing T. Recent observations carried out at higher temperature show a small increase in the integrated intensity as T increases. Assuming that this increase in absorption is due to a short-range isotropic overlap dipole and fitting the theoretically calculated results to the experimental data, reasonable values are obtained for the magnitude and range of this dipole. The assumption is tested by calculating the corresponding spectral profiles, and it is found that these are in good agreement with the experimental measurements over the temperature range 190 K to 350 K.

1. Introduction

In a series of papers presented some years ago, experimental measurements were made of the collision-induced absorption in the fundamental bands for N₂–N₂, O₂–O₂ and N₂–O₂ pairs [1–3]. Most of this absorption (approximately 90%) arises from the long-range quadrupolar induction mechanism, although there are smaller contributions mainly visible in the wings of the bands due to hexadecapolar induction. More recently, more accurate experimental measurements at room temperature revealed a ripple-like structure most visible in the plateau region in the S-branch [4]. Such features have been seen previously at lower temperature and attributed to bound dimers [5, 6]. After exploring unsuccessfully other mechanisms [2], we gave in [7] an analysis of the ripple structure in terms of a small contribution to the absorption by metastable dimers.

Most of the existing experimental data and theoretical analyses were carried out for temperatures of 300 K or lower. It is well known [8] that, as the temperature

decreases, the collision-induced linewidths decrease (the spectral band narrows), and for N₂–N₂, O₂–O₂ and N₂–O₂ pairs, the integrated intensity increases. This is consistent with our findings and with those of all previous work devoted to these systems as cited in [1–3], that most of the intensity arises from long-range induced dipoles. The corresponding temperature dependence arises from a Boltzmann average over separations between the centres of mass R of the colliding molecules. The dimensionless integrals are of the form

$$I(T) = 4\pi \int \frac{1}{x^{2L}} e^{-(\varepsilon/kT)((1/x^{12})-(1/x^6))} \mathrm{d}x, \qquad (1)$$

where $L = 3$ and 4 for the quadrupolar and hexadecapolar induction, respectively; $x = \sigma/R$, and ε and σ are the Lennard–Jones parameters for the colliding pair. Both these integrals decrease monotonically as T increases.

Recently, new measurements [9] at temperatures up to 353 K have shown that the integrated intensity for O₂–O₂ is relatively flat for T between 240 K and 300 K, but then rises significantly as T increases. Such a T-dependence has been observed previously for the

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fundamental band of H_2–H_2 [10]; however, for that system, it is well known that the isotropic overlap dipole contributes significantly in the Q-branch region [8, 11]. In order to model the observed T-dependence, Vigasin [12] proposed an oversimplified model which totally ignores the conventional expansion of the induced dipoles in a complete set of spherical harmonics of the orientations [13] and considers only a short-range isotropic overlap dipole. Then both the high- and low-T behaviours are explained in terms of that mechanism only, ignoring the well-known fact that the vast majority of the absorption arises from the long range quadrupolar mechanism.

In the present paper, using the usual expansion of the induced dipole [8, 13], we consider the effects of including short-range overlap dipoles in addition to the long-range collision-induced dipoles that are known to give reasonable agreement for $T < 300$ K; this agreement is not only for the integrated intensities, but also for the corresponding band profiles. In section 2, we present our analysis, and show the effects of these dipoles. Section 3 discusses the differences between the present approach and that of Vigasin [12], and gives the conclusions drawn from this work.

2. Theory for the collision-induced fundamental absorption band for O_2–O_2 pairs

Theoretical expressions for the various induced dipole moments and the methods used to calculate the integrated absorption and the band profiles have been discussed previously [1–3]. As a first step, we consider only the long-range quadrupolar components, previously found to account for most ($\approx 90\%$) of the absorption, characterized by

$$A_2(203; R) = \frac{\sqrt{3}}{R^4} Q_{01} \alpha_{00},$$

and

$$A_2(023; R) = -\frac{\sqrt{3}}{R^4} Q_{00} \alpha_{01}, \qquad (2)$$

where Q_{00} and Q_{01}, and α_{00} and α_{01} are the pure rotational and fundamental matrix elements of the quadrupole moment and the isotropic polarizability, respectively; R is the separation between the centres of mass of the two molecules. The integrated intensity S (in $cm^{-2} agt^{-2}$) can be written [1–3] as

$$S = \int \frac{1}{\rho_{O_2}^2} \alpha(\omega) d\omega = 4\pi^2 \alpha_F n_0^2 a_0^5 I(T) \{ Q_{01}^2 \alpha_{00}^2 + Q_{00}^2 \alpha_{01}^2 \} \omega_{iso},$$

$$(3)$$

where α_F is the fine structure constant, n_0 the number density at standard temperature and pressure, a_0 the Bohr radius, ω_{iso} is the intensity-weighted frequency that is close to the band centre, and $I(T)$ is the dimensionless integral calculated using equation (1) with $L = 3$ and the Lennard–Jones parameters ($\varepsilon/k = 128.8$ K and $\sigma = 6.353 a_0$) from Clifford *et al.* [14]. The results are presented in figure 1; from these one can see that this gives approximately 5–7% too much absorption for 190 K $< T < 300$ K. By decreasing slightly either the pure rotational matrix element of the isotropic polarizability α_{00} or the fundamental quadrupole moment Q_{01} (within their experimental uncertainties), one can easily get reasonable agreement for $T < 300$ K. In previous work [2], we also investigated the effects of including a short-range anisotropic overlap dipole having the same angular symmetry as the dominant long-range quadrupolar component $A_2(203; R)$, namely,

$$A_2(203; R) = \frac{\sqrt{3}}{R^4} Q_{01}\alpha_{00} + \mu_3 e^{-(R-\sigma)/\rho_3}, \qquad (4)$$

where μ_3 and ρ_3 are the strength and range of the overlap dipole. Although neither of these parameters is known, we previously assumed $\rho_3 = 0.11\sigma$ and found that a value of $\mu_3 = -2 \times 10^{-5} ea_0$ gave slightly better agreement in the plateau region, but that the overall agreement was not improved appreciably [2]. Note that because the A-components appear as squares, there is a destructive interference between the long- and short-range parts; thus by increasing the magnitude of μ_3 we will lower the corresponding absorption. The important point here is not that we can adjust the value of the integrated intensity, but rather to investigate the T-dependence of such a component given by the integral

$$I(T) = 4\pi \int \left[\frac{\sqrt{3}}{x^4} Q_{01}\alpha_{00} + \mu_3 e^{-\sigma(x-1)/\rho_3} \right]^2$$
$$\times e^{-(\varepsilon/kT)((1/x^{12})-(1/x^6))} x^2 dx. \qquad (5)$$

Because the magnitude of the quadrupolar term in equation (5) is much larger than that of the short-range overlap term, the square of the latter is negligible and the cross- product will have a T-dependence similar to that of the square of the first term. As a result, the integrated intensity will decrease but the T-dependence will not change appreciably. This is illustrated in figure 2 where we assumed a value $\mu_3 = -9 \times 10^{-5} ea_0$ in order that the theoretical integrated intensity is slightly lower than the observed values for low T.

In the next step, we subtract the two curves in figure 2 and obtain $S_{obs} - S_{the}$ and present the results in figure 3.
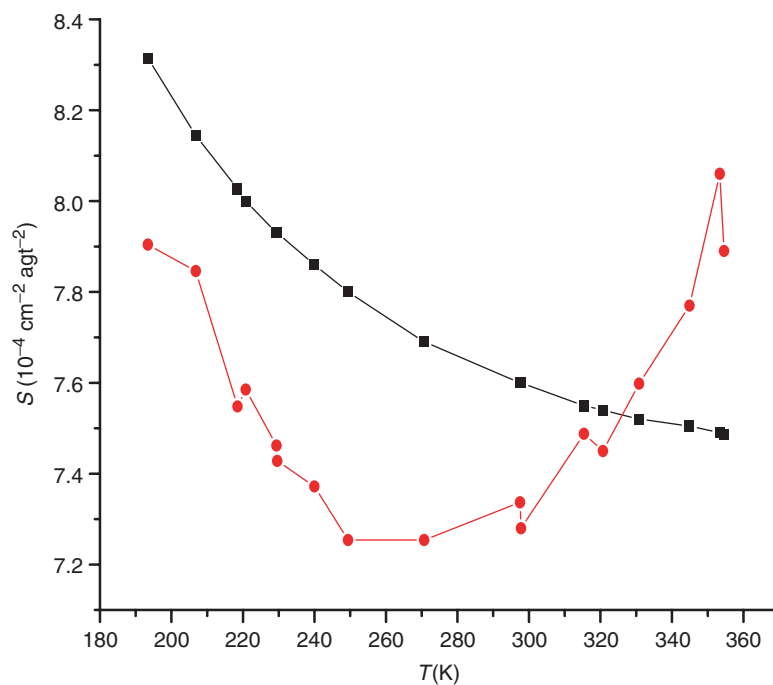
Figure 1. The integrated intensity S as a function of temperature T; the squares are the theoretical values calculated using equation (3), and the circles are the experimental data of Baranov *et al*. [9].
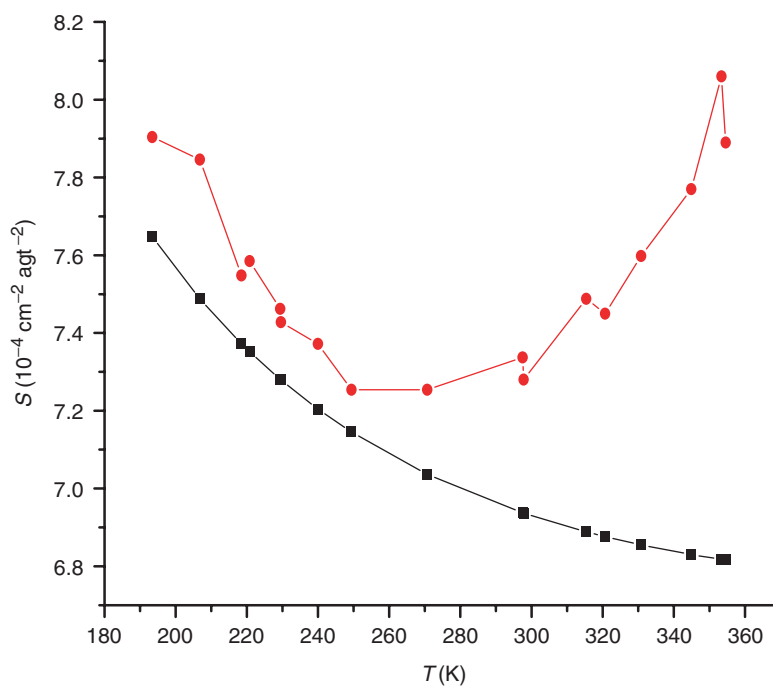

Figure 2. As figure 1 except the theoretical values are calculated using the component $A_2(203; R)$ with the short-range anisotropic overlap dipole given in equation (4).

This is the magnitude and *T*-dependence that we attribute to the isotropic collision-induced dipole described by the $A_0(001)$ coefficient $(8, 11, 13)$ having the form

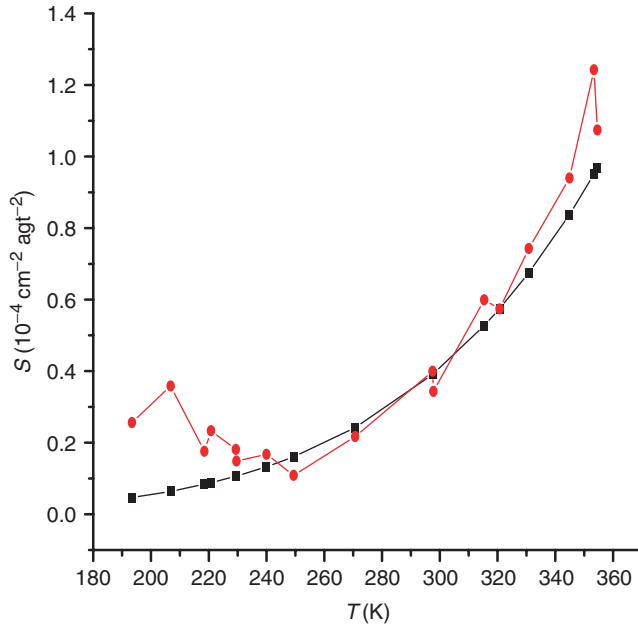$$A_2(001; \ R) = \mu_1 e^{-(R-\sigma)/\rho_1}, \qquad (6)$$

Figure 3. Comparison between the difference of the two curves in figure 2 (circles) and theoretical values (squares) calculated including the short-range isotropic overlap component given by equation (6); the magnitude and range of this dipole have been varied to give the best overall agreement.

where both the magnitude and range can, in principle, be different from those of the anisotropic (quadrupolar) overlap; this is the case in H_2–H_2 where accurate *ab initio* induced-dipole components have been calculated [11]. The *T*-dependence of this contribution is given by

$$I(T) = 4\pi \int \mu_1^2 e^{-2\sigma(x-1)/\rho_1} e^{-(\varepsilon/kT)((1/x^{12})-(1/x^6))} x^2 \mathrm{d}x. \quad (7)$$

By varying both μ_1 and ρ_1, we find that for the values $|\mu_1| = 1.543 \times 10^{-5} ea_o$ and $\rho_1 = 0.02\sigma$, we can get reasonably good agreement with the results shown in figure 3. Unlike the $A_2(203)$ component (equation 4), there is no long-range contribution for this dipole and the sign does not matter. As can be seen from the figure, the isotropic overlap contribution to the integrated intensity is small at low *T* but increases monotonically with *T*, accounting for approximately 15% of the observed absorption at $T = 350$ K. Finally, we present in figure 4, a comparison of our theoretical absorption with the observed results. Given the experimental errors [9] and the theoretical approximations, we regard the agreement as good.

In order to verify that the magnitude and *T*-dependence obtained for the isotropic overlap contributions are consistent with the observed profiles, these have been calculated at several temperatures. To accomplish this, the same line-shape is adopted for the quadrupolar contributions as used previously [2]; for the overlap contributions occurring in the Q-branch, we used a width larger by a factor of 3. Results for $T = 193$ K, 270 K, and 353 K are shown in figure 5(a)–(c), respectively, together with experimental profiles [9]. As can be seen, the agreement is reasonable, given the
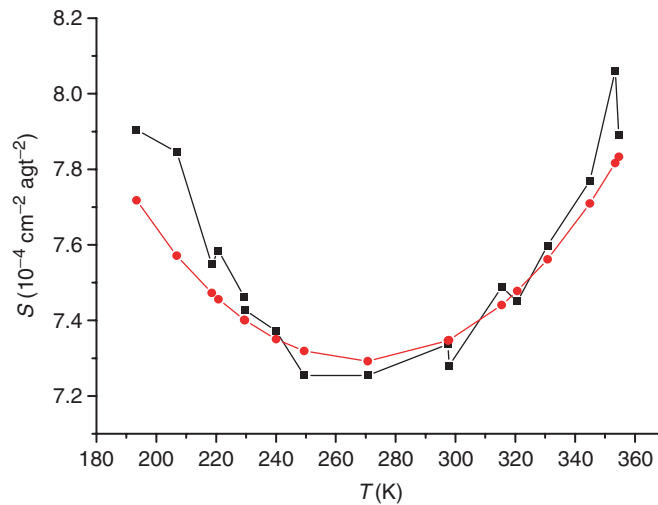

Figure 4. Comparison between the experimental data [9] for *S* as a function of *T* (squares) and the sum of the theoretical contributions (circles) shown in figures 2 and 3.
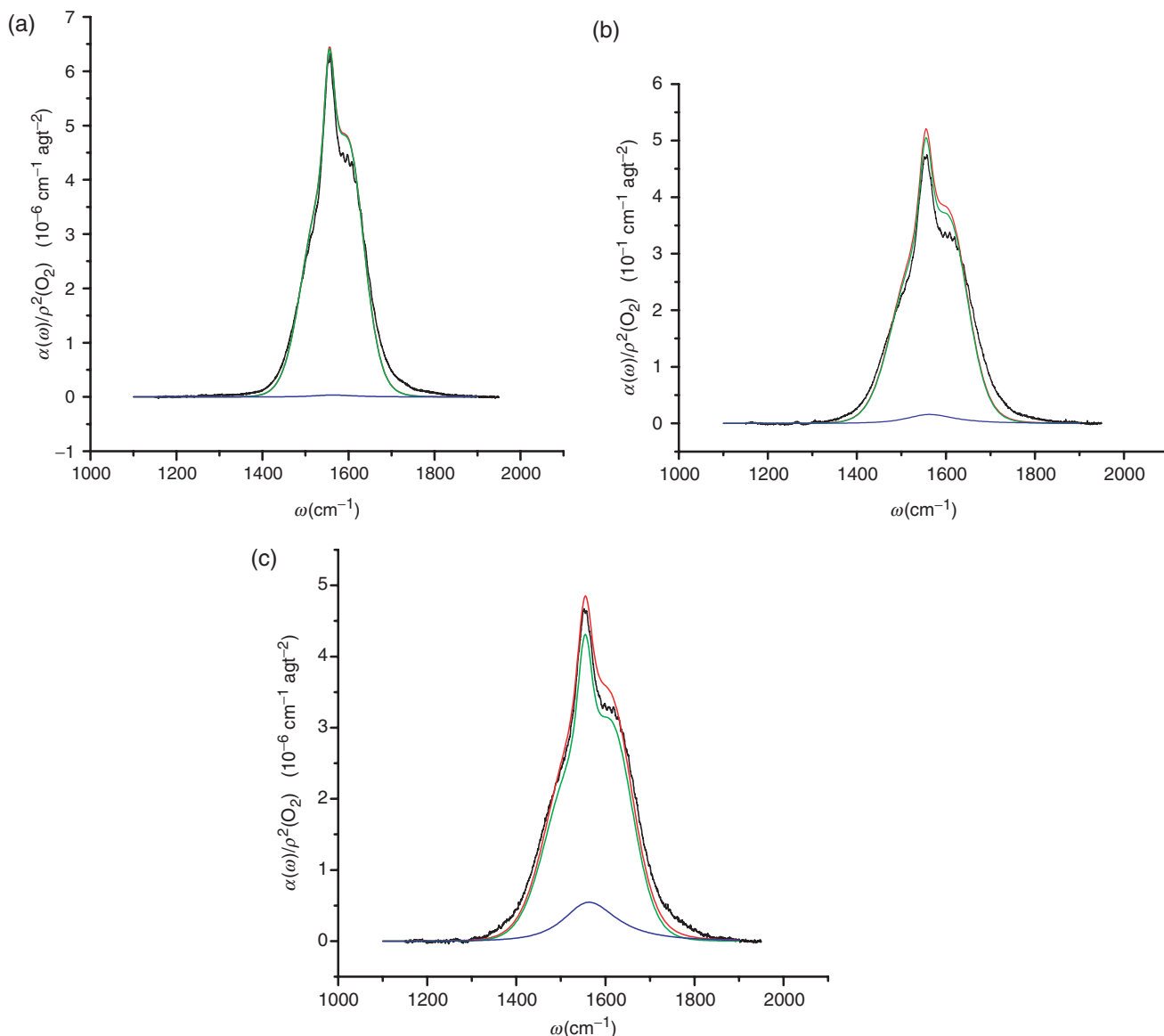
Figure 5. Band profiles $\alpha(\omega)/\rho^2$ (O_2) *versus* ω for three T: (a) 193 K; (b) 270 K; (c) 353 K. The experimental curves show the ripple structure, while the lowest curve is the theoretical isotropic overlap contribution; the other two curves are the theoretical quadrupolar contribution and the total.

unknown parameters for the overlap dipoles. If accurate *ab initio* values were available, one could make more extensive theoretical calculations for comparison with experiment. However, in the present work, we have not made any attempt to optimize the agreement, because we feel that this is unwarranted at present.

3. Discussion and conclusions

In the present study, it has been shown that most of the observed integrated absorption for the collision-induced fundamental band of O_2–O_2 arises from the long-range

quadrupolar mechanism. The increase in this absorption for $T > 270$ K is most likely due to the isotropic overlap dipole contribution; this contribution increases monotonically with T.

This is in sharp disagreement with the results of Vigasin [12] who attributed all the T-dependence to an isotropic overlap dipole, the square of which he wrote as

$$\mu(R)^2 = \mu_0^2 e^{-\alpha(R-R_0)}, \tag{8}$$

where μ_0, α, and R_0 are adjustable parameters. This assumption ignores the known T-dependence of the dominant quadrupolar absorption. He obtained two

expressions for the T-dependence of the integrated intensity I_{high} at high T (which he defined as when all the vibrational states in the potential well are equally populated) and I_{low} at low T. The resulting temperature integrals contain four adjustable parameters: R_{e}, α, ε/k, and R_0. (Note that by 'normalizing' the T-dependence, the magnitude of the overlap moment μ_0 never enters.) Then by adjusting all four parameters, he obtained the functions I_{low} and I_{high} of T that decrease and increase, respectively, with increasing T. However, the range parameter R_0 obtained is anomalously small (0.001 Å), while the Lennard–Jones values for R_{e} and ε/k are not in good agreement with measured values [14]. Finally, in order to obtain a T-dependence comparable with experiment, he independently scaled his two functions so that the sum is 1 at $T = 200$ K. Without scaling independently, the curves I_{low} and I_{high} calculated using his parameters cross close to 220 K not near 400 K as shown in his figure 2. Moreover, a dipole limited to only an isotropic overlap contribution would result in absorption in the Q branch and would not be able to explain the observed profiles that obviously contain O and S lines as well.

In the present work, the largest contribution to the intensity at all temperatures considered, arises from the long-range quadrupolar induction mechanism. The magnitude of the integrated intensity is affected by the introduction of a short-range anisotropic overlap component, although the T-dependence is not significantly changed. We attribute the observed increase at temperatures above 300 K to an isotropic overlap dipole component, described by the coefficient $A_0(001;R)$ given in equation (6). Its contribution to the absorption is very small for $T < 280$ K, but increases rapidly with increasing T so that for $T = 350$ K, it accounts for approximately 15% of the total absorption. By varying the magnitude and range for this mechanism, we can get good agreement with reasonable values for these parameters. However, because no independent quantitative data are known for this dipole, our present results must be regarded as tentative.

As a complementary test of the consistency of the model, we also calculated band profiles, and obtained reasonable agreement over the range $T = 193$–353 K, using reasonable values for the line-shape parameters.

Again, we are well aware of the speculative nature of this work, which was undertaken mainly to stimulate the interest of theoreticians. The accuracy now achieved by the experimental data and the even finer details observed, requires *ab initio* calculations such as those that have been made for the simpler system H_2–H_2 [11]. When available they will enable a more extensive analysis of both the magnitude of the integrated intensity and the T-dependence. For that purpose,

experimental measurements at higher T would also be helpful.

Finally, because of the importance of O_2 in the Earth's atmosphere, and for future searches for Earth-like extrasolar planets, it is important to achieve a detailed, quantitative understanding of its spectroscopic properties. In this regard, we reiterate that it would be useful for *ab initio* calculations of the collision-induced dipoles for O_2–O_2 to be carried out, not only for vibration–rotation transitions, but also for electronic transitions as well [15, 16].

Acknowledgements

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